Supplementary Information for

High-contrast fluorescence sensing of aqueous Cu(I) with triarylpyrazoline probes: Dissecting the roles of ligand donor strength and excited state proton transfer

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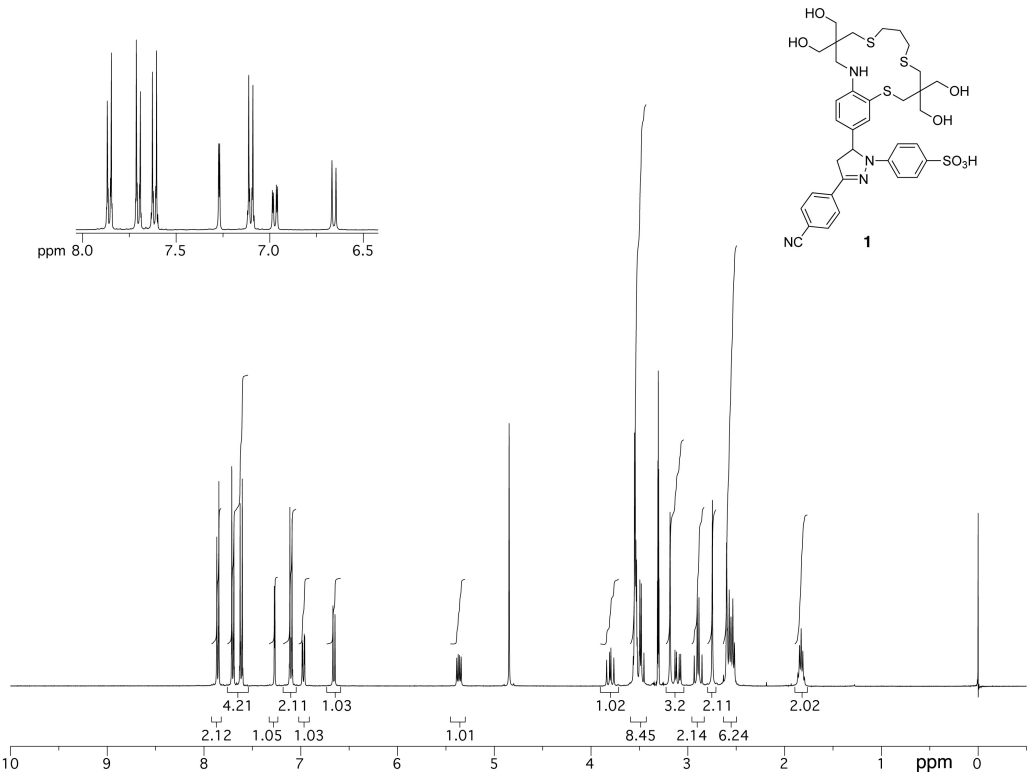
^{1}H-NMR (CD_3OD, 400 MHz)



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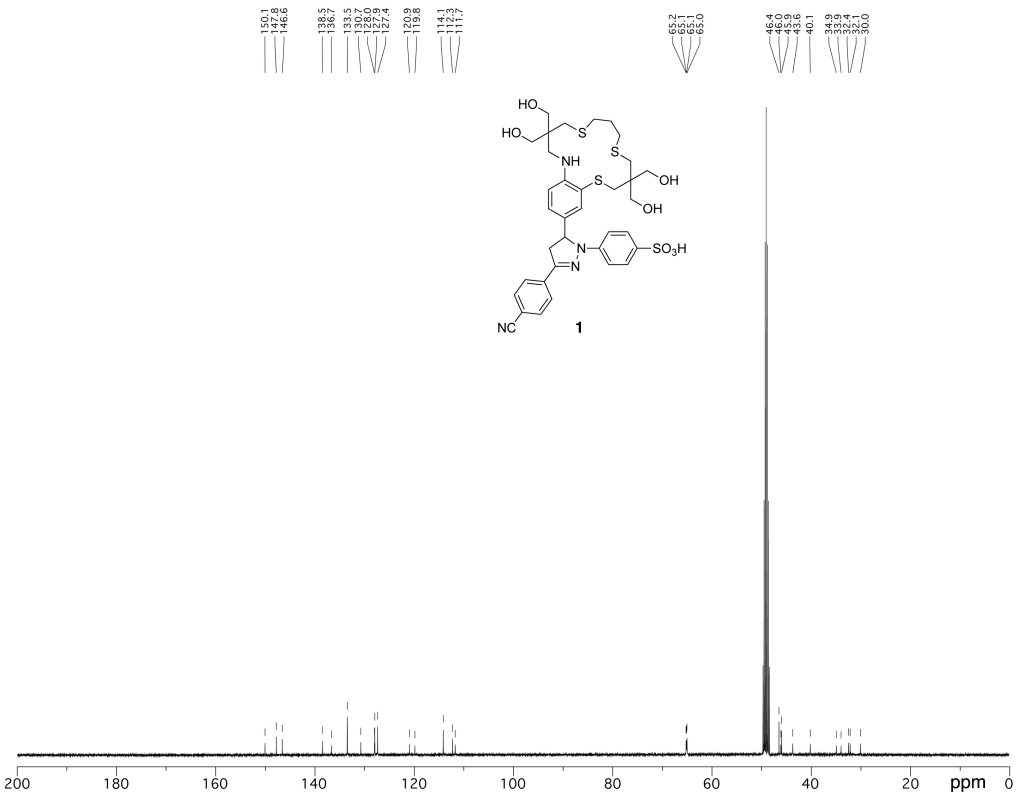

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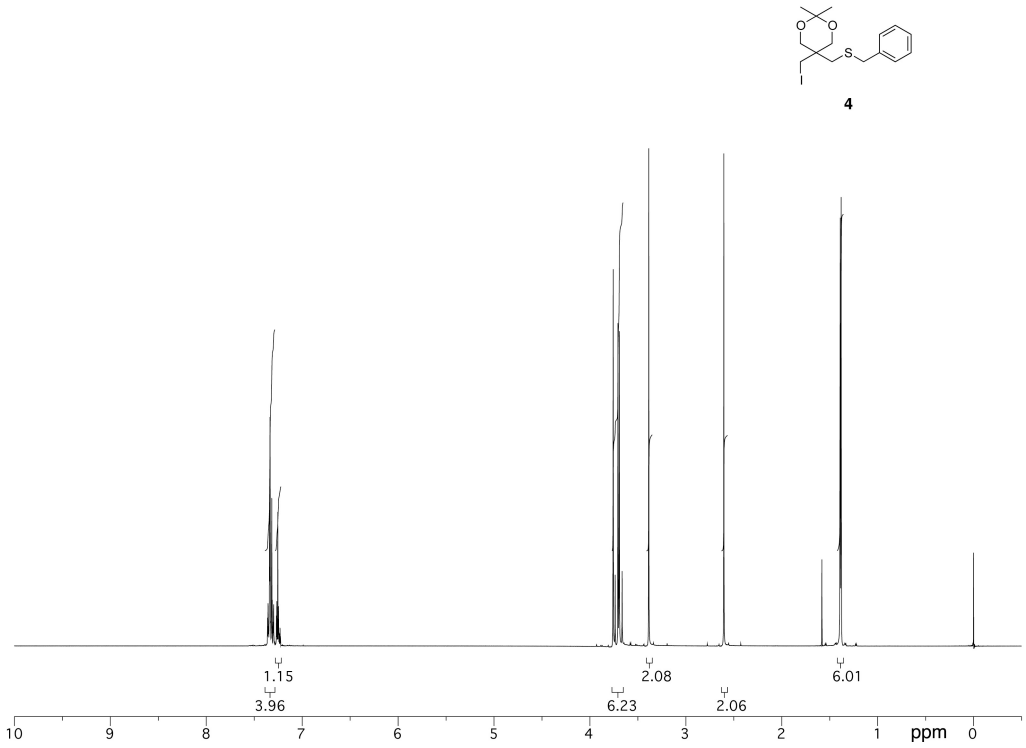

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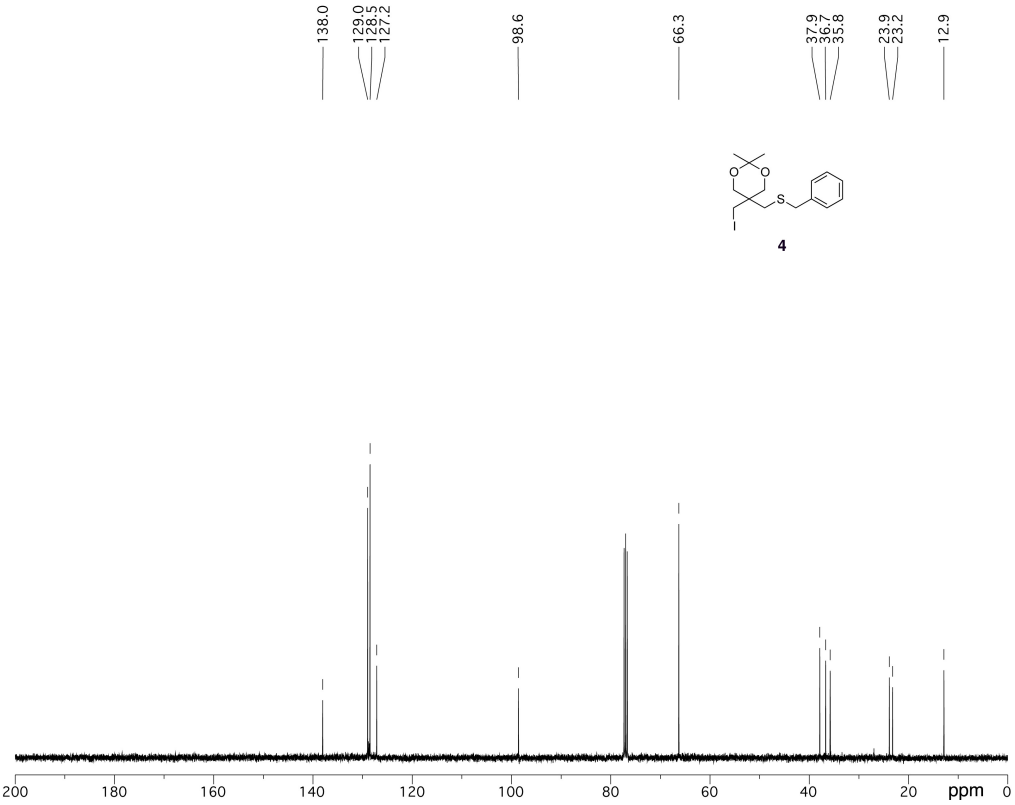

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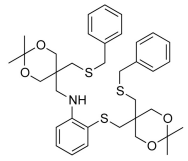

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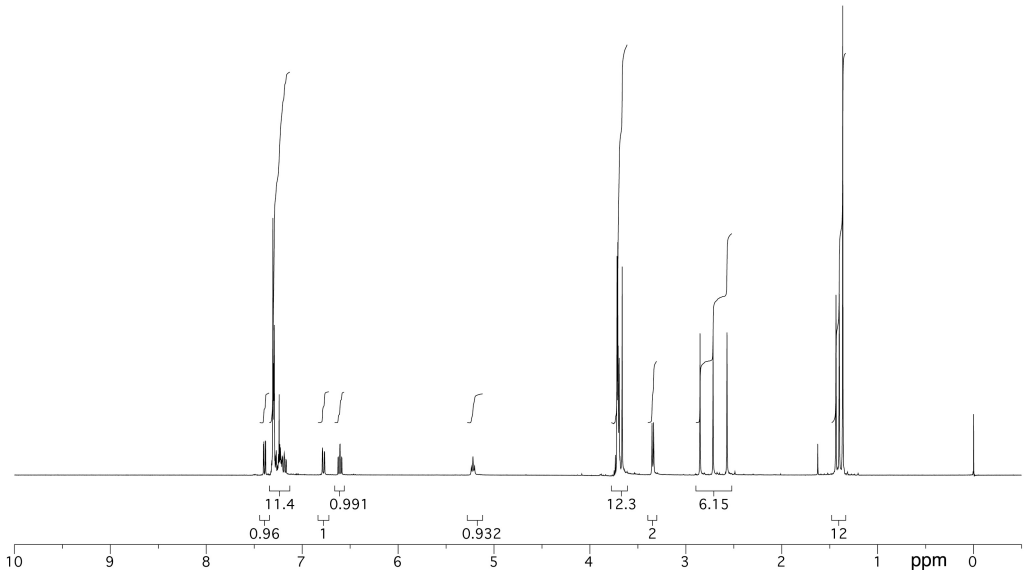

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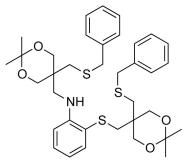

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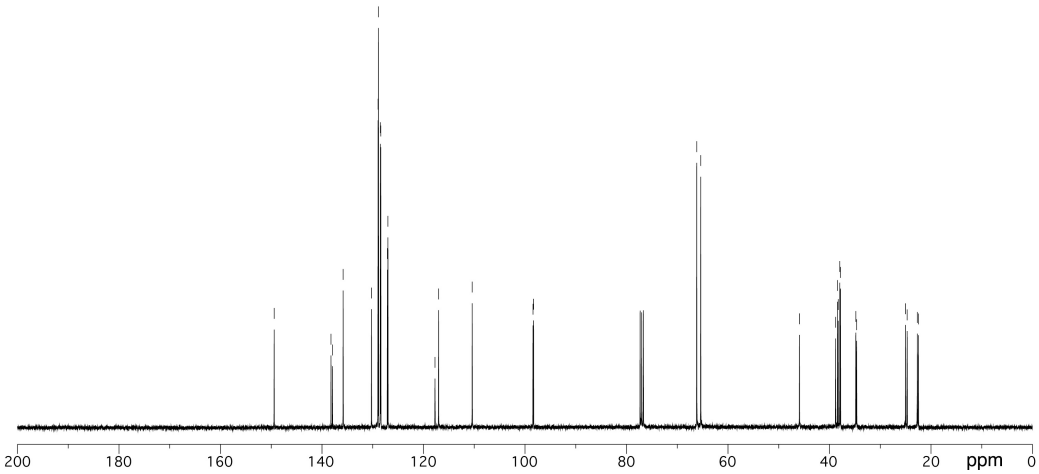

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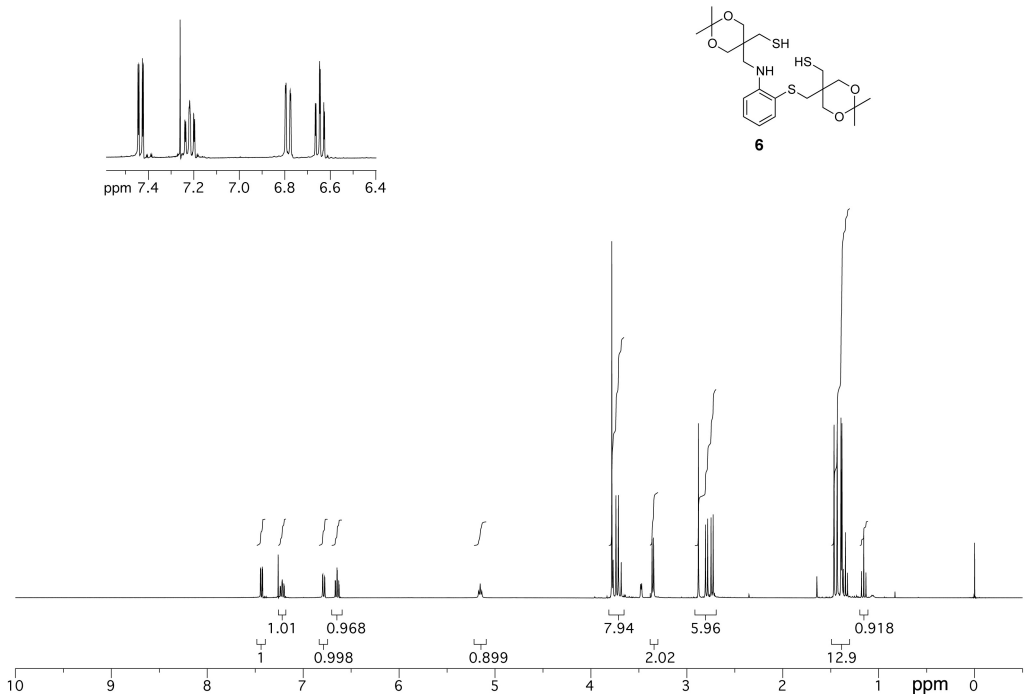

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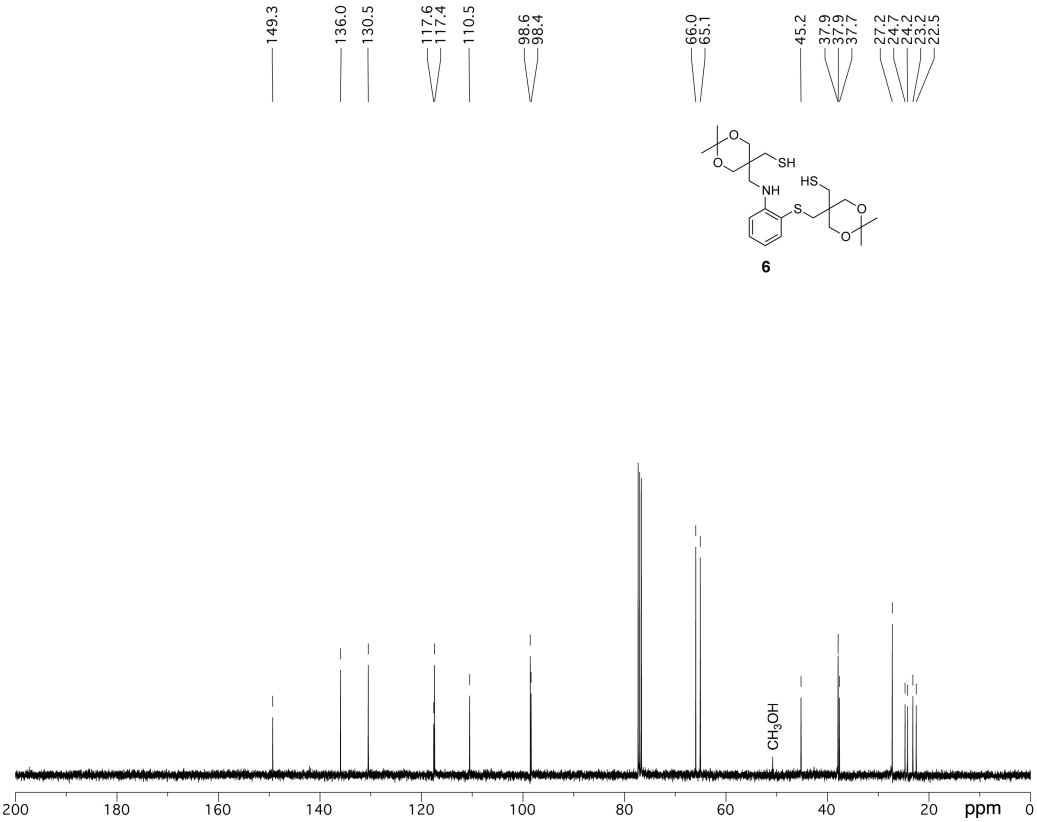

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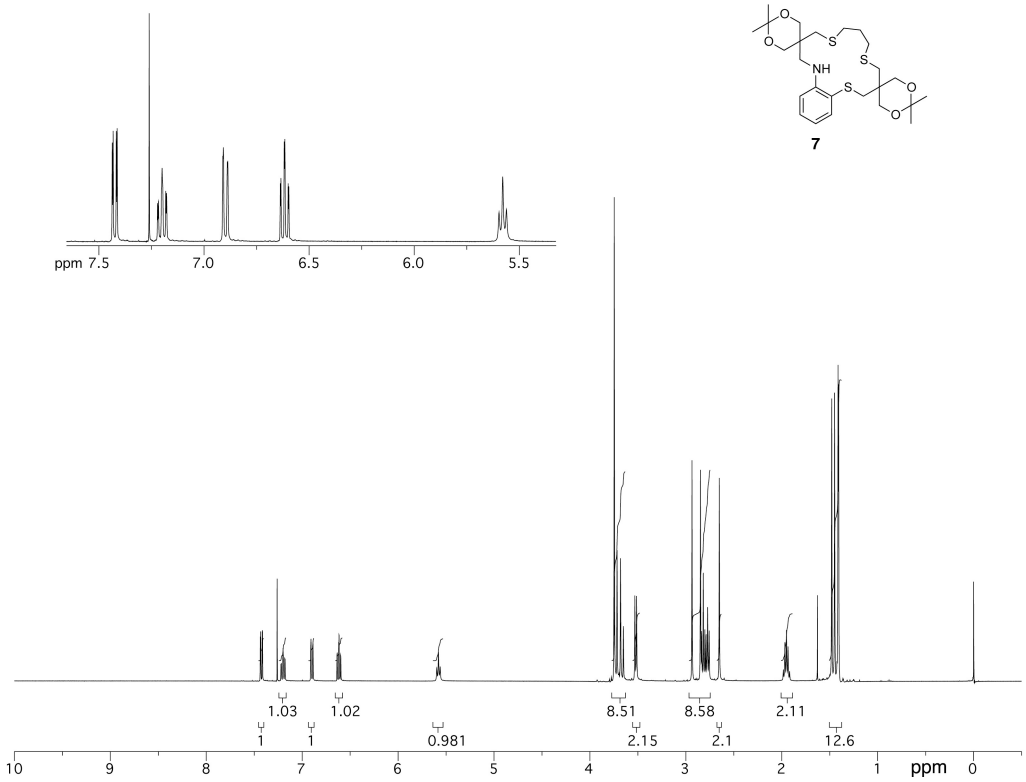

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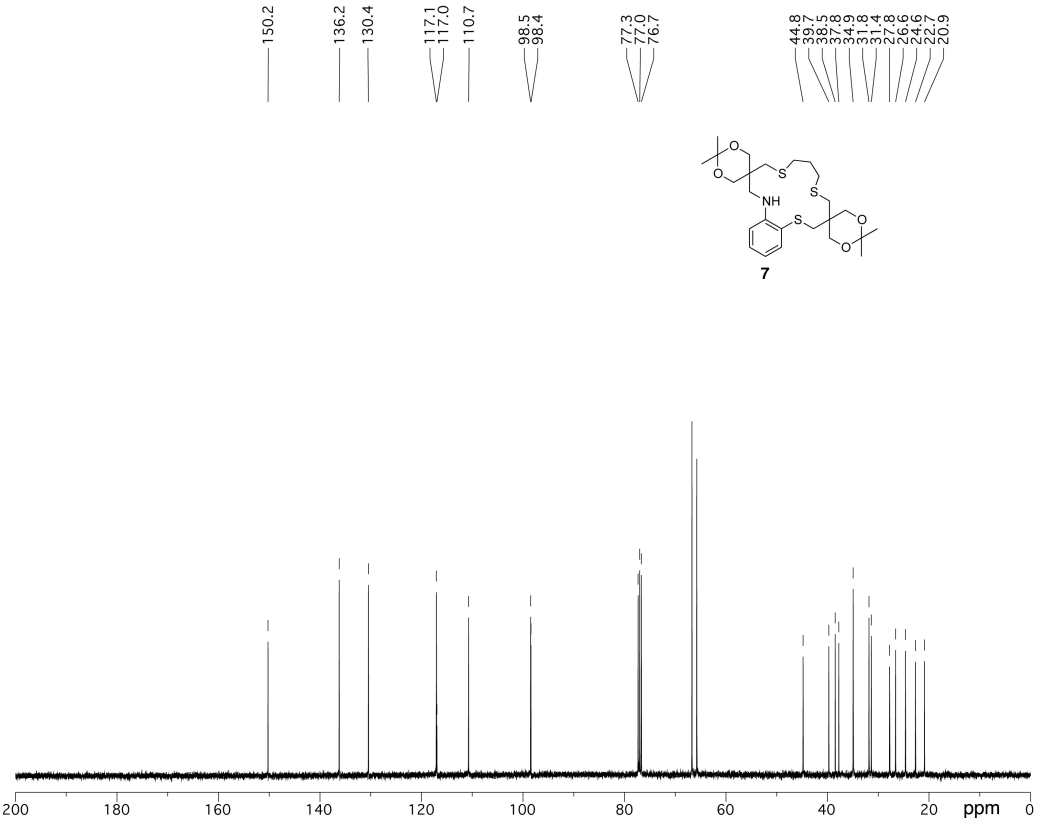

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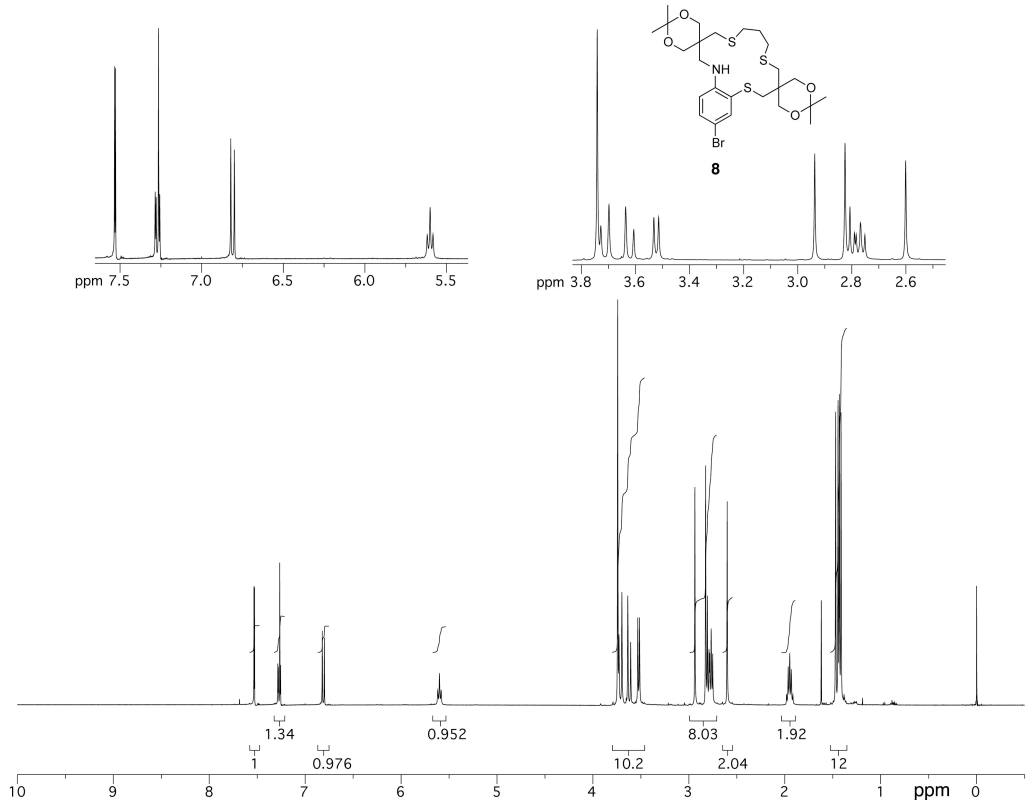

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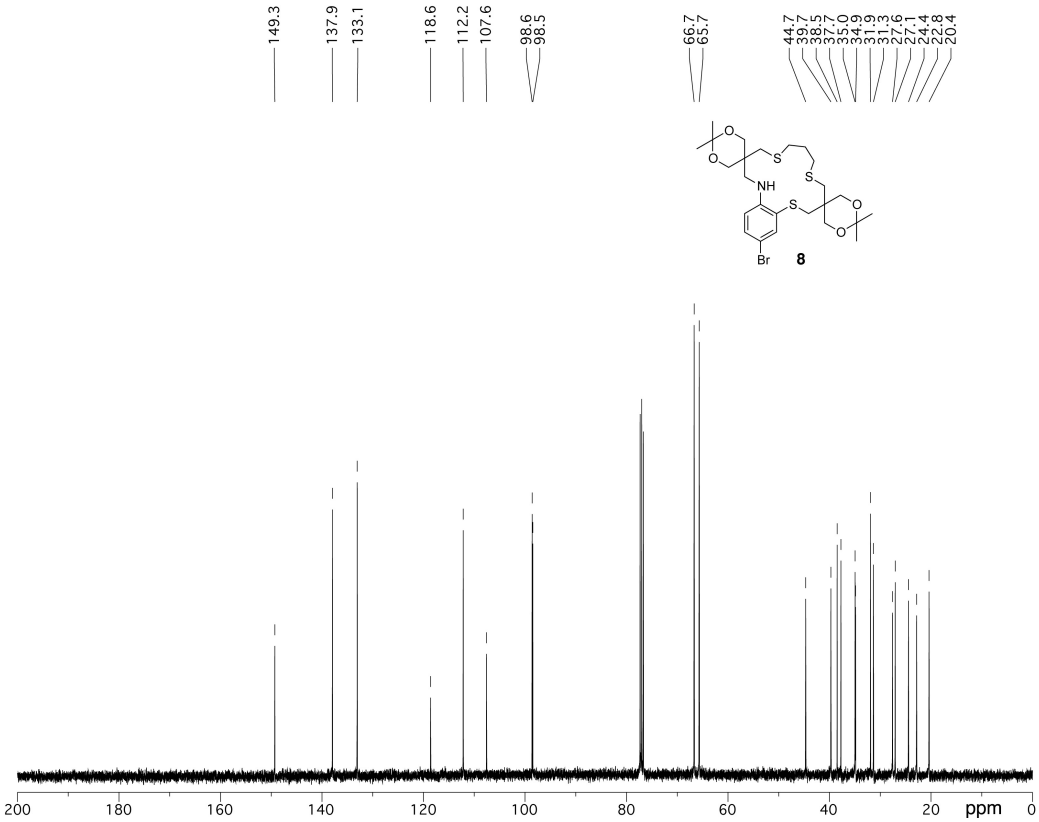

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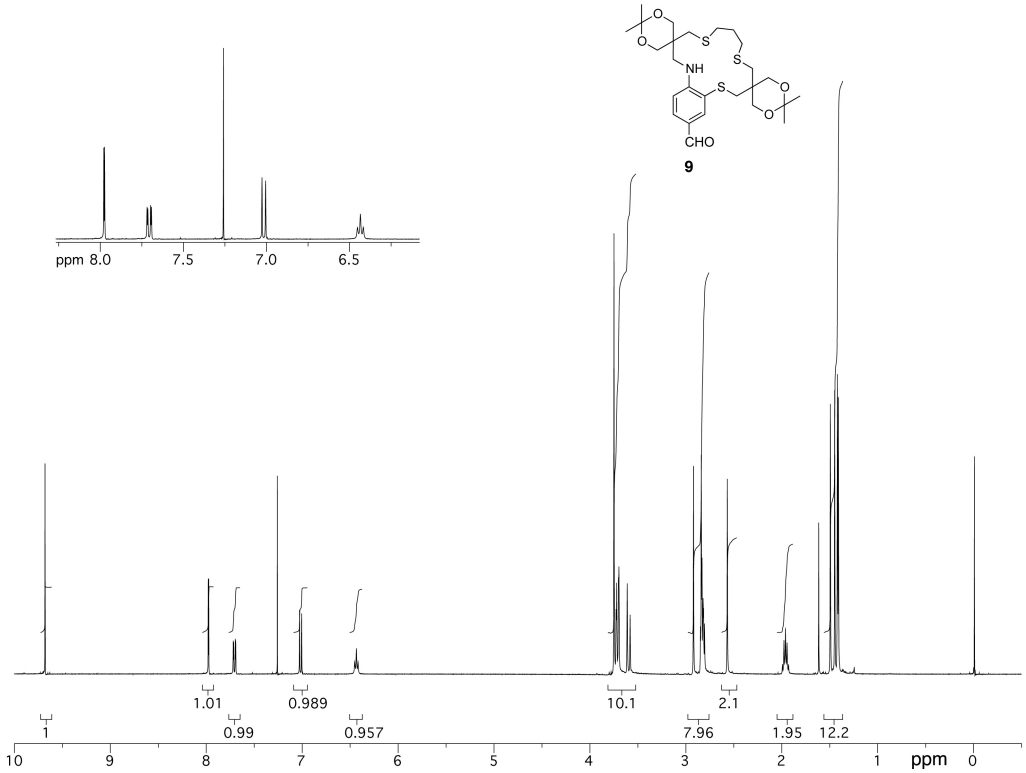
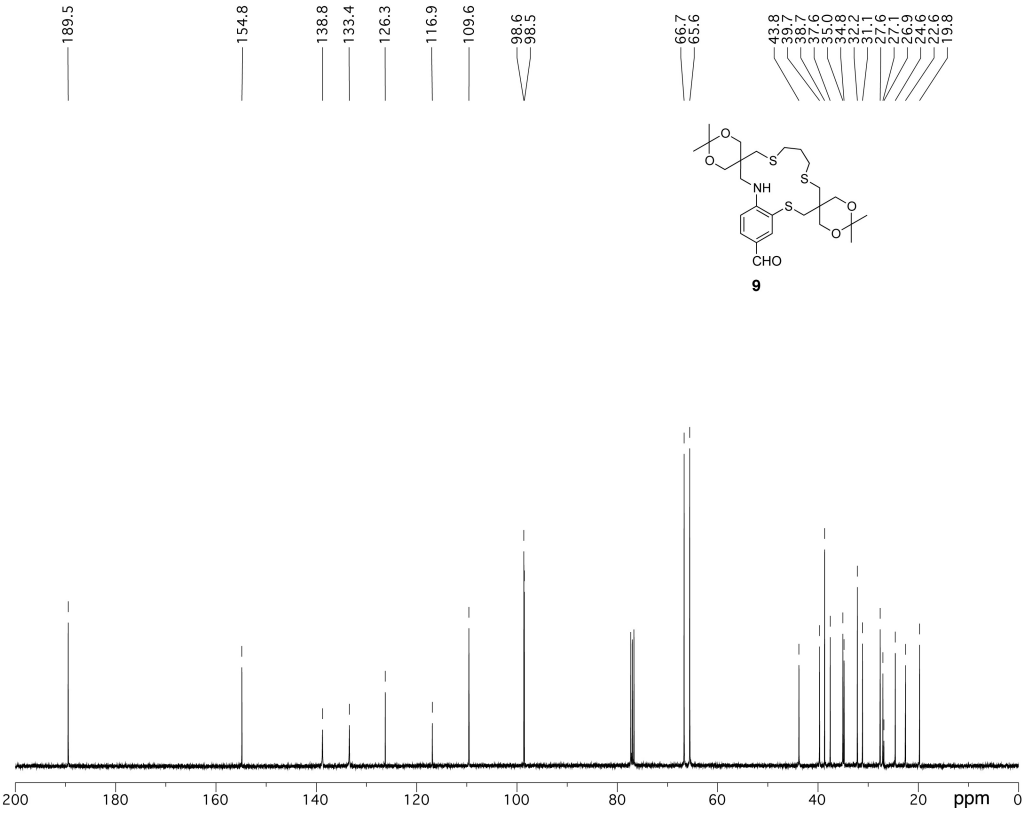
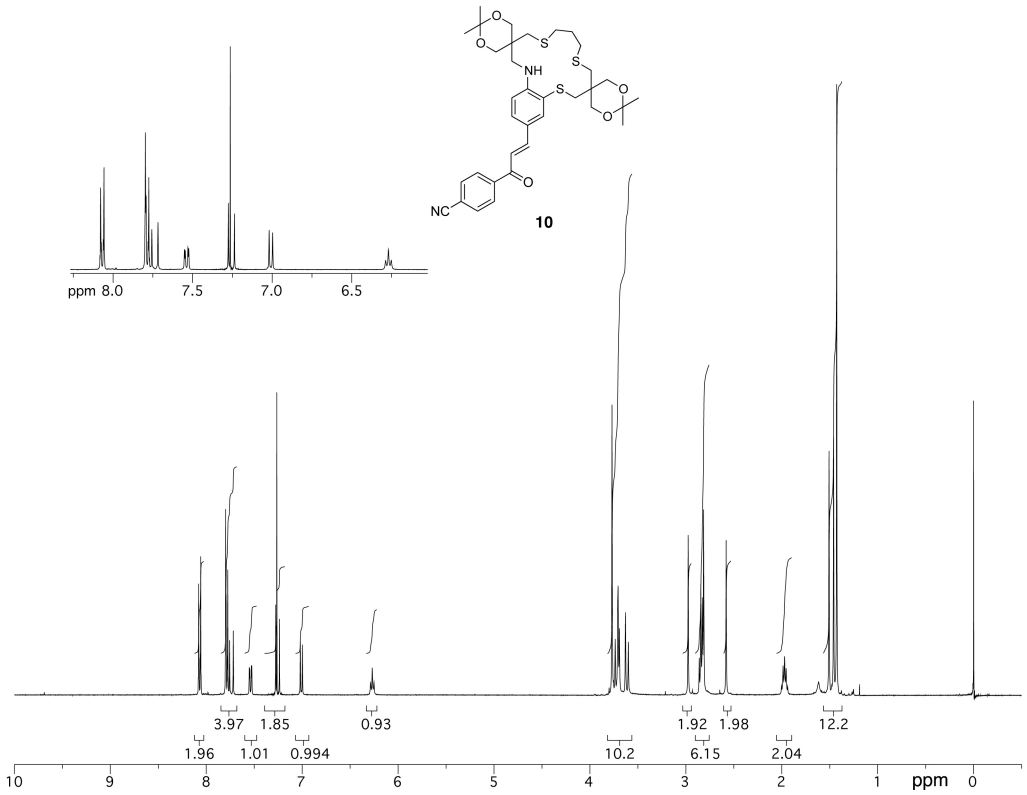


^{13}C-NMR ($CDCl_3$, 100 MHz)



^{1}H-NMR ($CDCl_3$, 400 MHz)



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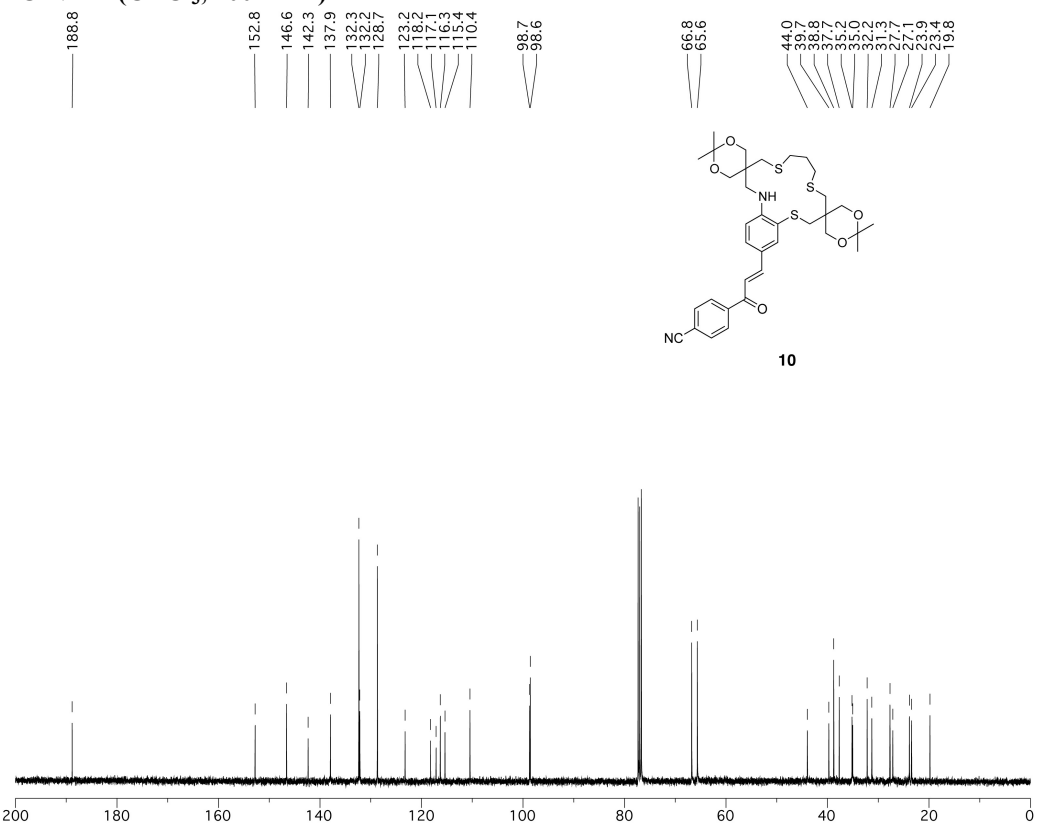
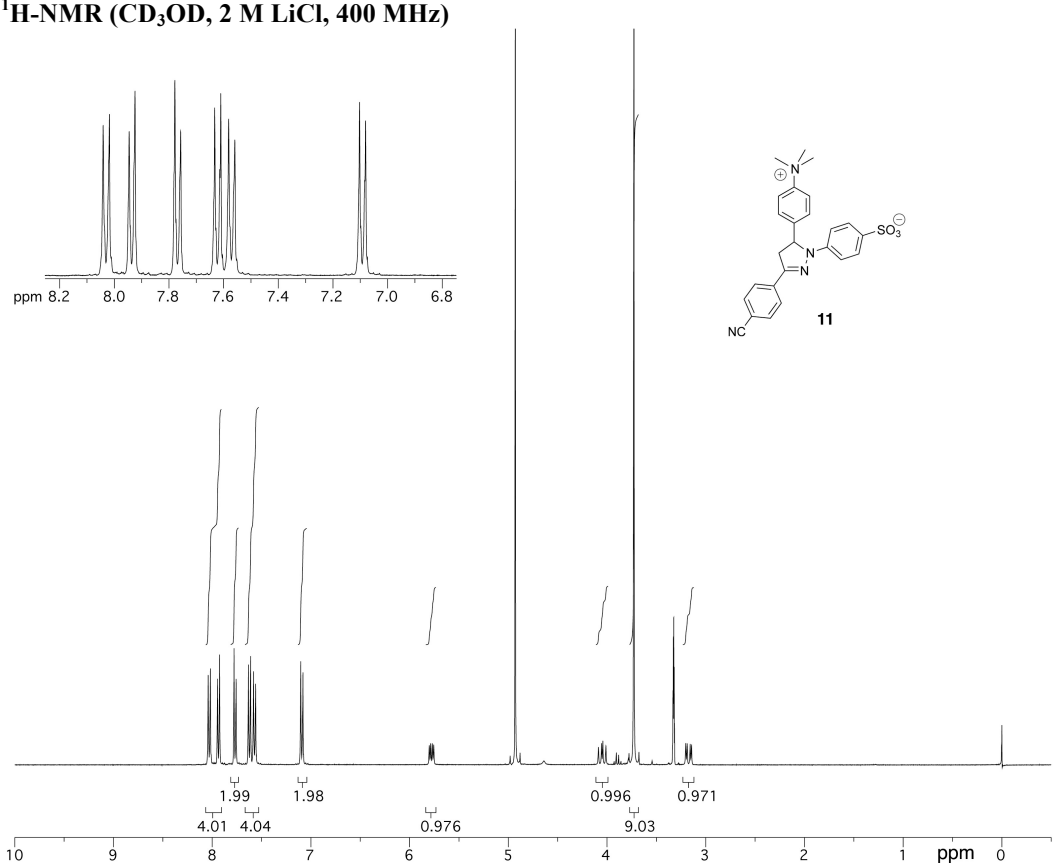


^{1}H-NMR (CD_3OD, 2 M LiCl, 400 MHz)



Note: the quartet near 3.8 ppm is due to residual 2,2,2-trifluoroethanol used as solvent in the preparation of **11**.

2. Time-resolved Fluorescence Emission Decay Data

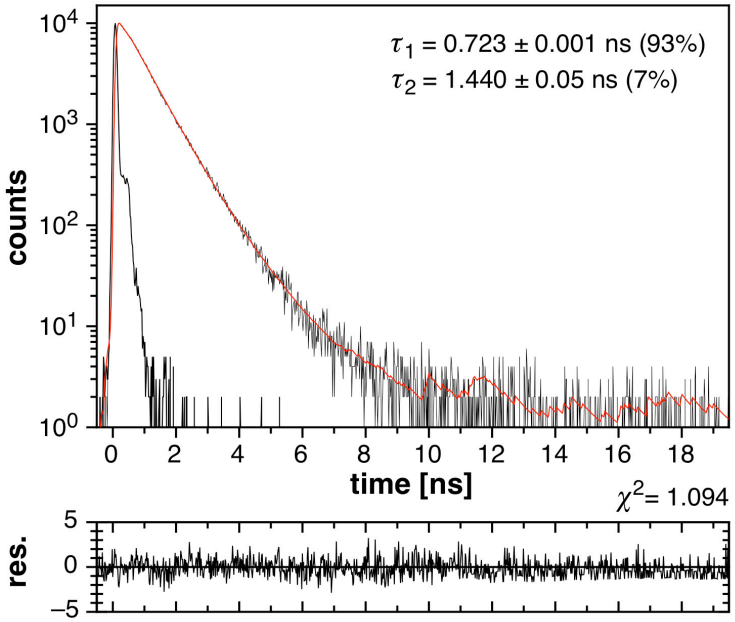


Figure S1a: Fluorescence decay profile for pyrazoline derivative **1** in aqueous buffer (10 mM MOPS/K^+, pH 7.2) at 22 °C (IRF = instrument response function; curve fit for a biexponential decay shown as solid trace in red).

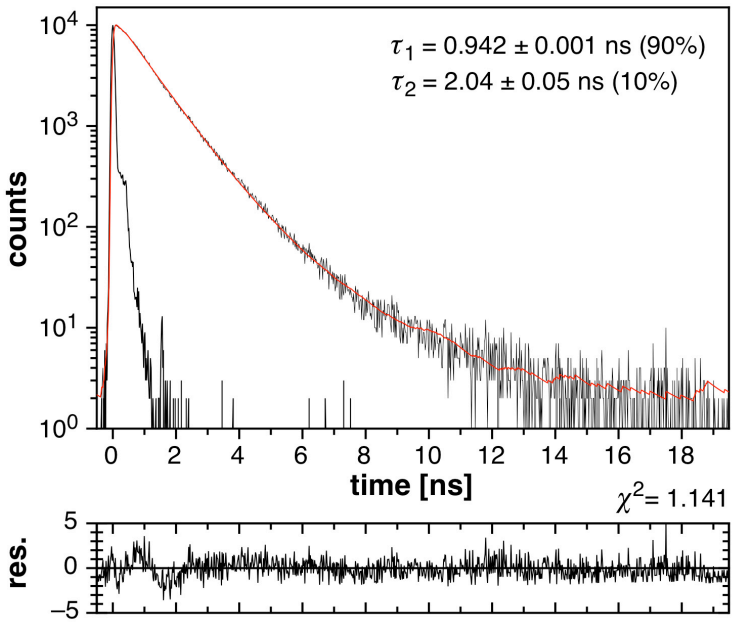


Figure S1b: Fluorescence decay profile for pyrazoline derivative **1** in D_2O buffer (10 mM MOPS/K^+, pH* 7.3 in D_2O corresponding to pH 7.2 in H_2O) at 22 °C (IRF = instrument response function; curve fit for a biexponential decay shown as solid trace in red).

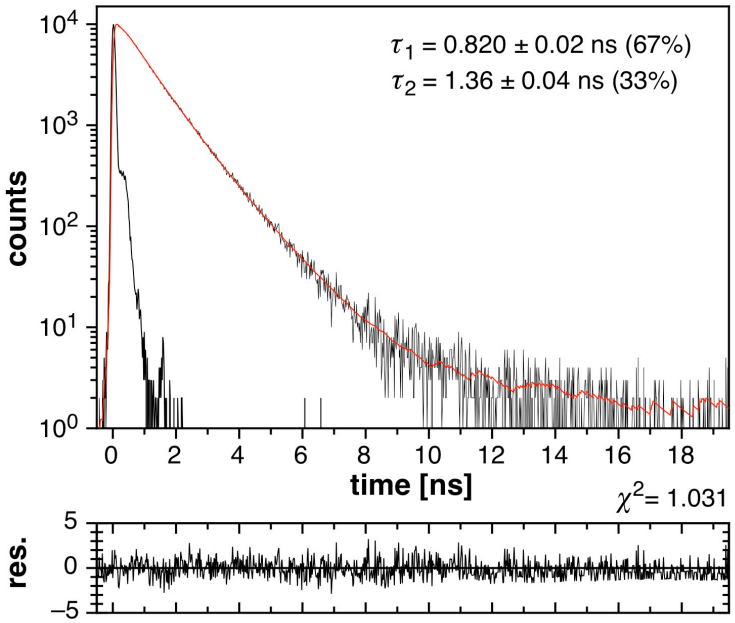


Figure S2: Fluorescence decay profile for pyrazoline derivative CTAP-2 in aqueous buffer (10 mM MOPS/K^+, pH 7.2) at 22 °C (IRF = instrument response function; curve fit for a biexponential decay shown as solid trace in red).

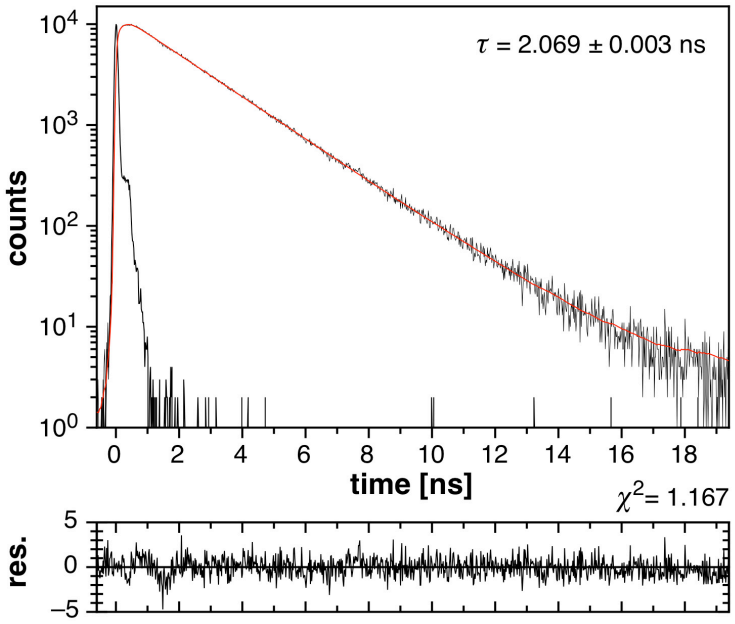


Figure S3a: Fluorescence decay profile for pyrazoline derivative **11** in water at 22 °C (IRF = instrument response function; curve fit for a monoexponential decay shown as solid trace in red).

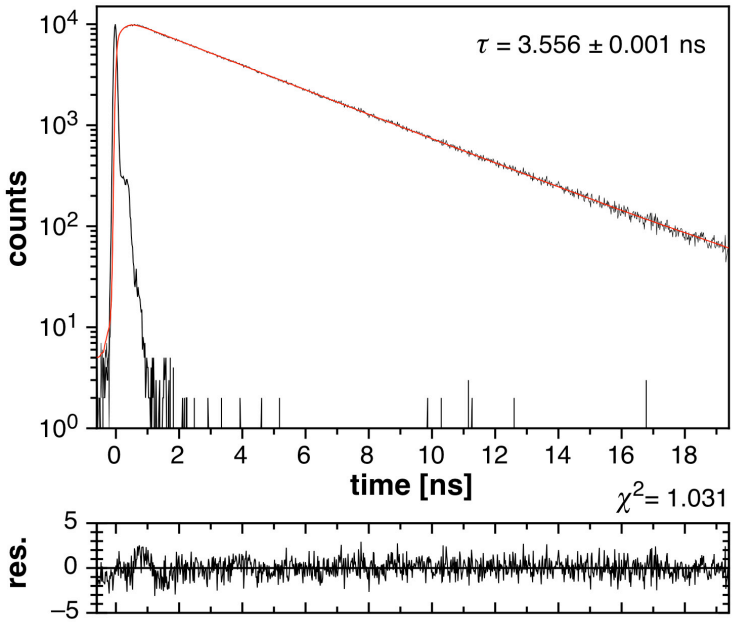


Figure S3b: Fluorescence decay profile for pyrazoline derivative **11** in D_2O at 22 °C (IRF = instrument response function; curve fit for a monoexponential decay shown as solid trace in red).

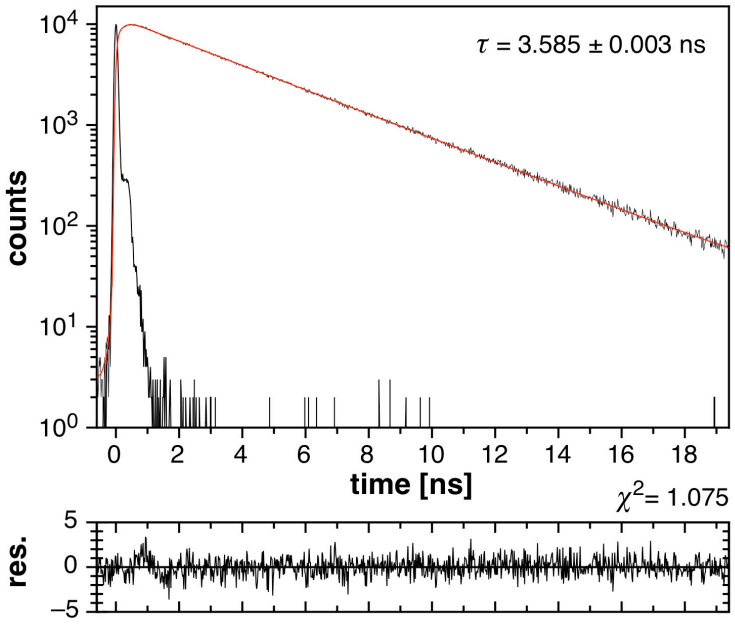


Figure S3c: Fluorescence decay profile for pyrazoline derivative **11** in MeOH at 22 °C (IRF = instrument response function; curve fit for a monoexponential decay shown as solid trace in red).

3. Electrochemistry

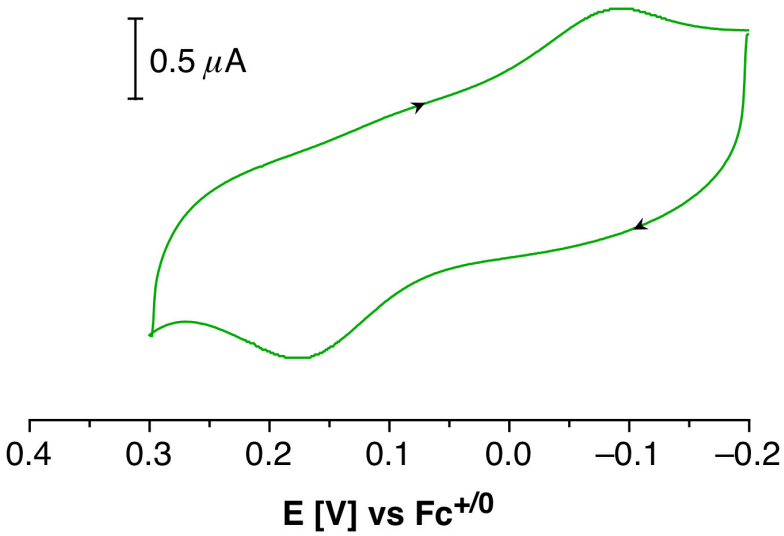


Figure S4: Cyclic voltammogram of **1** (70 μM) in the presence of 30 μM $[Cu(I)(CH_3CN)_4]PF_6$ at pH 5.0 under deoxygenated condition (10 mM PIPBS, 0.1 M $KClO_4$, glassy carbon working electrode, Pt counter electrode, aqueous Ag/AgCl/1 M KCl reference electrode, scan rate 50 mV/s, direction indicated by black arrows). The voltammogram was referenced against the external $Fc^{+/0}$ potential measured under the same conditions.

4. Determination of the Apparent Cu(I)-Affinity of Probe 1

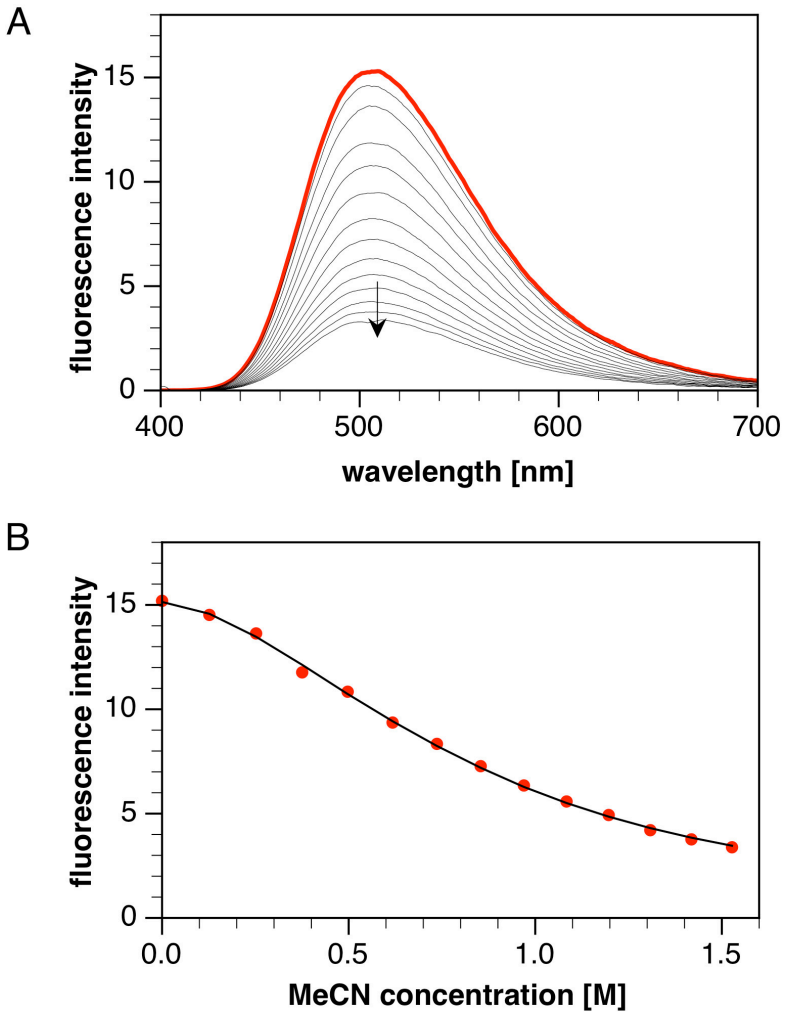


Figure S5: Fluorescence titration of pyrazoline **1** (5µM) with CH_3CN in the presence of 3.6 µM $CuSO_4$ and 50 µM sodium ascorbate under deoxygenated condition in PIPBS buffer (50 mM, pH 5.0, 60 mM $KClO_4$, 22°C). A) Fluorescence spectra acquired for c(CH_3CN) ranging between 0 to 1.60 M. The red trace corresponds to the emission spectrum prior to addition of CH_3CN. B) Fluorescence intensity change (red points) and curve fit (solid trace) for the titration (A) at a wavelength of 508 nm (log $K^{Cu(I)} = 9.71 \pm 0.02$).

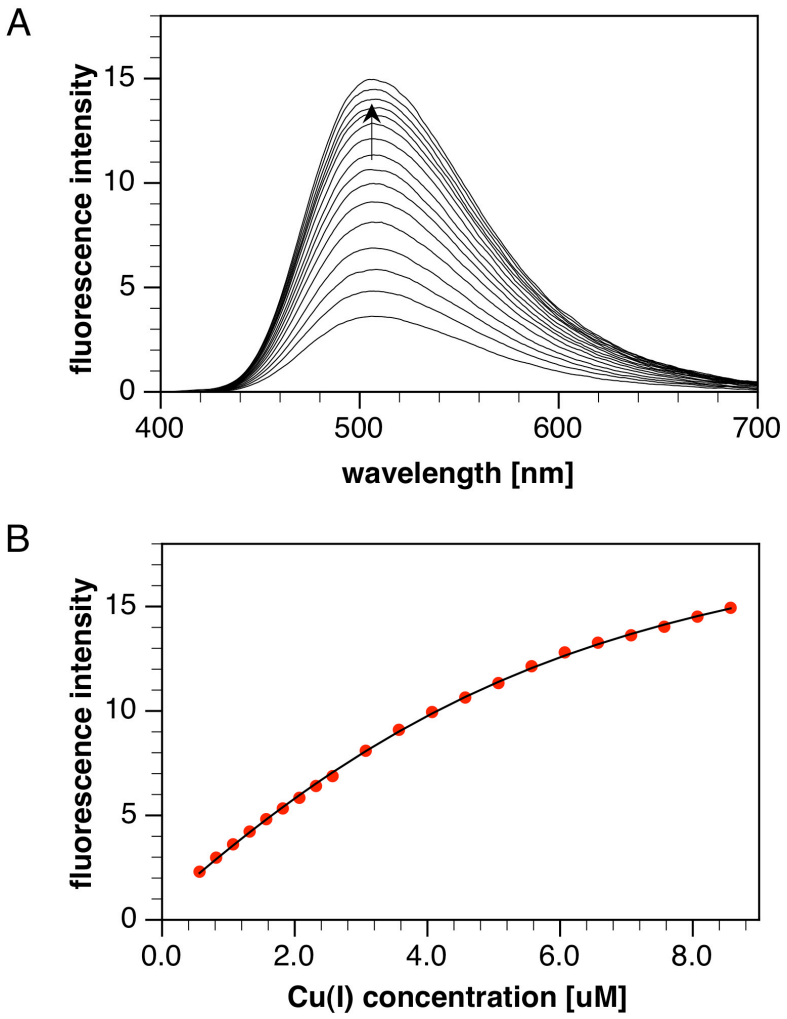


Figure S6: Fluorescence titration of pyrazoline **1** (5 μM) with $CuSO_4$ in the presence of 100 μM sodium ascorbate and constant CH_3CN concentration of 0.70 M under deoxygenated condition in PIPBS buffer (50 mM, pH 5.0, 60 mM $KClO_4$, 22°C). A) Fluorescence spectra acquired for c(Cu(II)) ranging between 0.56 to 8.56 μM. B) Fluorescence intensity change (red points) and curve fit (solid trace) for the titration (A) at a wavelength of 508 nm (log $K^{Cu(I)} = 9.74 \pm 0.03$).

5. Determination of the Acid Dissociation Constant of Probe 1

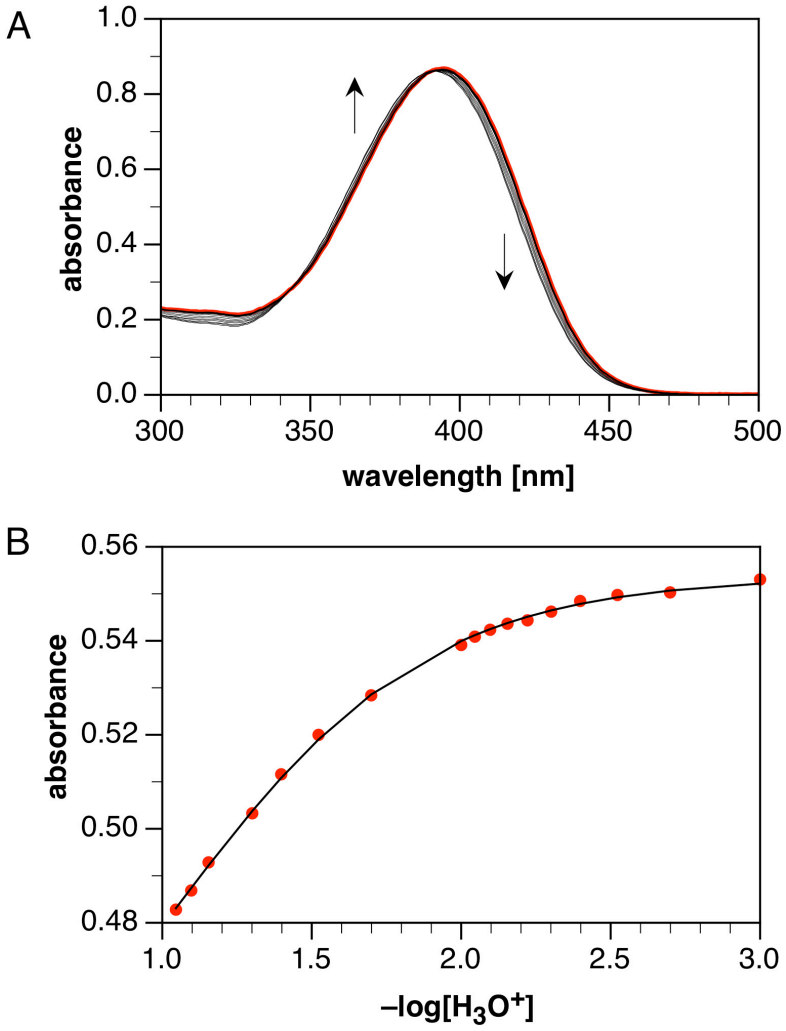


Figure S7: Titration of pyrazoline **1** with HCl at constant 0.1 M ionic strength. A) UV-vis spectra acquired for c(HCl) ranging between 1 mM to 100 mM. The red trace corresponds to the UV-vis absorption spectrum at $-\log[H_3O]^+ = 3.0$. B) Absorbance change (red points) and curve fit (solid trace) for the titration (A) at a wavelength of 419 nm ($pK_a = 1.0 \pm 0.05$).